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A Micromechanics Approach for Attachment and Detachment of Asymmetric Colloidal Particles

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ABSTRACT

Particle detachment is the initial step in colloid mobilization, and this process needs to be understood thoroughly for more accurate estimates of colloid facilitated contaminant transport in streams and groundwater. In this study a micromechanics interaction model has been developed for kaolinite particles, and experiments have been performed on attachment and detachment of particles in porous media columns. The experimental results are discussed and interpreted in terms of microscopic forces, in contrast to conventional computations in the colloid literature which are based on energy terms. The force calculations are done using expressions developed for the natural shape (hexagonal platelets) of the kaolinite particles without making use of unrealistic assumptions of particle sphericity. The forces considered are van der Waals forces, electrical double layer forces, hydration forces and Born repulsion. The interparticle force calculations have been used to analyze different modes of association of kaolinite platelets as a function of pH. Under constant chemical conditions the three likely modes of interaction of kaolinite platelets showed significantly different total force curves. The microscopic force analysis was found to be consistent with experimental results.

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INTRODUCTION

Bed sediments of many natural water bodies are polluted by non-point and point sources of contaminants. These contaminants are often adsorbed to cohesive bed sediments. During episodic events with changes in hydrodynamic and colloidal forces, contaminant-laden cohesive bed sediments are detached and resuspended followed by transport. Puls and Powell (1992) emphasized that a three phase approach to contaminant transport models should be adopted instead of the conventional two-phase approach. The mobile fluid phase and the immobile solid phase are considered in two-phase transport models. The consideration of a third phase, which incorporates a mobile solid phase, is however necessary under many hydrogeochemical conditions (Puls and Powell, 1992). Puls and Powell (1992) reported that the rate of colloid-assisted arsenate transport was 21 times greater than that of the dissolved arsenate. In another study radioactive Cesium (^{137}Cs) transport through soil was found to be primarily controlled by sorption onto colloidal clay particles followed by particle transport (Torok et al., 1990). In such cases, neglecting the contaminant transport via colloid mobility could lead to serious underestimation of contaminant mass flux.

Particle detachment is the initial step in colloid mobilization. It is a physico-chemical process which occurs when hydrodynamic forces or physico-chemical forces or both overcome adhesive interparticle forces. In most cases, a mechanistic understanding of the detachment phenomenon is a prerequisite to the precise estimation of colloid-facilitated transport of contaminants. Particle detachment is also important in understanding floc breakup, in current theories of deep-bed filtration, and in backwashing of filters. The focus of this paper is on theoretical developments.

BACKGROUND

In the past, attempts have been made to explain colloid release using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Kuo and Matijevic, 1978), which predicts an infinitely deep primary minimum and a corresponding infinite adhesive force at separation distances approaching zero. In reality an infinitely strong attraction is unlikely because short-range effects such as those caused by ion hydration and Born repulsion keep particles from coming into atomic contact. When a particle is attached to the surface of a media grain, the distance between their surfaces approaches an equilibrium separation distance of approximately 0.3 to 1 nm (Derjaguin et al., 1975; Overbeek, 1977). Therefore, during its detachment a deposited particle has to be pulled off from the primary minimum located 0.3 to 1 nm from the surface. At such small distances of separation additional non-DLVO forces influence the primary minimum and DLVO theory fails to explain particle detachment (Raveendran and Amirtharajah, 1995). However, if non-DLVO forces like Born repulsion and hydration forces are considered the depth of the primary minimum not only becomes finite but also dependent on chemistry of the interacting aqueous medium (Ruckenstein and Prieve, 1976; Raveendran and Amirtharajah, 1995).

Colloid scientists have generally analyzed particle interactions using interaction energies rather than forces experienced by the particles. In practice, it is easier to deal with the potential energy of interaction between particles than the interparticle forces (Hunter, 1993). However, it is the forces between the macroscopic bodies that are often easier to measure, and of greater interest, rather than their interaction energies (Israelachvili, 1991). Significant differences have been shown to occur between calculations made in terms of energy and in terms of forces at short separation distances (below 10 nm). Therefore, in order to develop a satisfactory model for particle detachment, the interparticle interactions have to be quantified in terms of forces instead of conventional energy terms (Raveendran and Amirtharajah, 1995). This would also allow the

incorporation of hydrodynamic forces in the total force calculations done in colloid mobilization studies. Raveendran and Amirtharajah (1995) analyzed detachment of spherical particles.

Kaolinite particles exist in nature as thin hexagonal platelets having two large flat faces and approximately rounded edges. The electrochemical properties of a face are markedly different from those of an edge. The cleavage planes (faces) of the platelets are negatively charged while the edges are positively charged under acidic conditions and the edge charge is pH dependent. With a hexagonal platelet representation, kaolinite particles may associate in three possible modes of interaction; namely, face-face (F-F), edge-face (E-F), and edge-edge (E-E). Because of the complex nature of kaolinite platelets, formulating a satisfactory interaction model for kaolinite platelets is difficult. Flegmann et al. (1969) developed an energy interaction model for kaolinite particles wherein the face surface is represented by a flat plate and the edges as a sphere. However, there exists microscopic evidence (Weaver, 1976) that edges of the kaolinite platelets are not flat but rounded like a half cylinder. James and Williams (1982) criticized the approach of Flegmann et al. (1969) and used DLVO theory alone to formulate an energy interaction model for kaolinite particles in which the platelet edges were represented by cylinders rather than spheres.

van der Waals Forces

On the basis of Hamaker's approach (Hamaker, 1937), the attractive energy between two particles may be calculated by integration of the attractive energies from all atomic pairs formed by two atoms belonging to different particles. Based on the Hamaker method the potential energy of attraction per unit area between two flat plates of thickness, δ , is given by Verwey and Overbeek (1948) as

$$E_v = \frac{-A}{12\pi} \left\{ \frac{1}{z^2} + \frac{1}{(z+2\delta)^2} - \frac{2}{(z+\delta)^2} \right\} \quad (1)$$

where z is the distance of closest approach between two flat plates and A is the Hamaker constant.

Using Hamaker's summation method, Israelachvili (1991) developed an expression for the non-retarded van der Waals interaction energy between two parallel cylinders of radii r_1 and r_2 , and length ℓ which is given by

$$E'_v = -\frac{A\ell}{12\sqrt{2}z^{3/2}}\left(\frac{r_1 r_2}{r_1 + r_2}\right)^{1/2} \quad (2)$$

Using the concept of pairwise summation, Sparnaay (1959) developed an expression for the attractive potential energy between two parallel cylinders of equal radii, which was simplified by James and Williams (1982) to

$$E''_v = \frac{-A\ell}{24r}\left(\frac{r}{z}\right)^{3/2} \quad (3)$$

This expression is the same as the one developed by Israelachvili (1991) using Hamaker's method, and could be obtained easily by substituting $r_1 = r_2$ in Equation 2.

Electrical Double Layer Forces

At present, various aspects of electrical double layer interactions are unknown and the interparticle interactions are based on constant charge or constant potential assumptions (Elimelech et al., 1995). In general, the true situation lies somewhere in-between constant potential and constant charge interactions (Overbeek, 1977). A simple approach which offers a useful compromise between these two extremes is the Linear Superposition Approximation (LSA). The differences among the three approaches are most prominent at short distances of separation and the LSA always gives intermediate values (Gregory, 1975). Since neither constant charge nor constant potential is likely to be correct in practical situations, the LSA may be the most appropriate expression to describe reality. Using LSA, Gregory (1975) reported the

following expression for the electrical double layer repulsion energy between two flat plates at potentials ψ_1 and ψ_2 :

$$E_E^{LSA} = 32\varepsilon\kappa\left(\frac{kT}{e\nu}\right)^2 \tanh\left(\frac{e\nu\psi_1}{4kT}\right) \tanh\left(\frac{e\nu\psi_2}{4kT}\right) \exp(-\kappa z) \quad (4)$$

where ε is the permittivity of the medium, k is the Boltzmann constant, ν is the valence of an ion, κ is the Debye-Hukel parameter, and T is the absolute temperature.

Hydration Forces

Churaev and Derjaguin (1985) reported the structural component of the interaction energy per unit area between two parallel plates at a distance z apart to be given by

$$E_H = K h \exp\left(-\frac{z}{h}\right) \quad (5)$$

where K is the constant of the structural forces and h is the characteristic length of the structural forces.

Born Repulsion

A realistic formulation for Born repulsion, at least at the approximation level of the DLVO theory, would be the Hamaker-type integration of all molecules in the system (Elimelech et al., 1995). Using this approach Ruckenstein and Prieve (1976) developed a formula for sphere-plate Born repulsion

$$E_B = \frac{A\sigma^6}{7560} \left[\frac{8r+z}{(2r+7)^7} + \frac{6r-z}{z^7} \right] \quad (6)$$

in which the collision diameter σ is treated as a second characteristic property of the solids and typically has a value of the order of 0.5 nm.

THEORETICAL DEVELOPMENTS

A representative kaolinite platelet with two hexagonal flat faces and rounded edges is shown in Figure 1. Because of the electrokinetic properties of kaolinite platelets, situations may arise in which the face and edge sites have either opposite or similar signs of charge. Three modes of interparticle interaction, F-F, E-F, and E-E, are therefore possible depending upon the physico-chemical environment. Expressions have been developed for electrical double layer forces, hydration forces, and Born repulsion for the three likely modes of interaction of these asymmetric particles.

In most cases, coarse natural sediments are covered with layers of small deposited particles. Also in deep bed filtration, media grains exhibit multilayer coverage. The release of all of the particles deposited on the media grains is unlikely through filter backwashing (Amirtharajah, 1978). Therefore, in the development of a realistic conceptual model for particle detachment it is necessary to analyze the interaction between a single particle and a filter media grain coated with a deposited layer of particles (Raveendran and Amirtharajah, 1995). In this theoretical treatment the following assumptions have been made:

- Kaolinite particles are thin hexagonal platelets.
- The cleavage surfaces of the kaolinite platelets are flat and they can be represented by flat plates in interparticle force calculations.
- Platelet edges are rounded and their interaction is represented by half cylinders of radii equal to half the thickness of the platelet.
- Three kinds of interparticle associations are considered: namely, F-F, E-F, and E-E. The F-F interaction is represented by the flat plate-flat plate interaction, the E-F interaction is represented by the interaction between a flat plate and a cylinder parallel to it, and the E-E

interaction is modeled as the interaction between two similar parallel cylinders. Similar assumptions have also been made by James and Williams (1982).

Hydration Force

Face-Face Hydration Force

The hydration repulsion energy per unit surface area between two parallel flat surfaces can be transformed to force terms by differentiating Equation 5 with respect to separation distance z to yield

$$F_H^f = K \exp\left(\frac{-z}{h}\right) \quad (7)$$

Edge-Face Hydration Force

The edge-face interaction has been modeled as the interaction between a flat plate and a half cylinder parallel to it as shown in Figure 2. Interaction energy between a flat plate and a half cylinder of radius, r , is determined using Derjaguin's integration procedure (Derjaguin, 1934). This method has already been used for spherical particles (Israelachvili, 1991). The applicability of this method in the case of cylindrical particles may, for geometric reasons, be even better than the spherical particles (Sparnaay, 1959). In this method, the surface of the cylinder is thought to be divided into 'ribbons' of length, ℓ , and width, $rd\theta$, where ℓ and r are length and radius of the cylinder and the angle θ has been shown in Figure 2. If radius of the cylinder is much larger than the separation distance, z , then the total interaction energy between the two surfaces could be found by integration of a series of separate interactions between the flat plate and the individual strips of width $rd\theta$. As shown in Figure 2, the surface of the cylinder is divided into small strips of length ℓ and width $rd\theta$. The area of a small 'ribbon' dA is given by

$$dA = \ell r d\theta \quad (8)$$

If the distance of closest approach between the cylinder and the plate is given by z , then the variable distance Z between a small strip and the plate surface as a function of angle θ is given by

$$Z = z + r - r \cos \theta \quad (9)$$

Equations 5, 8 and 9 can be combined to get the hydration energy (dE_H) between a small strip of area dA and the flat plate as given by

$$dE_H = Kh \exp\left\{\frac{-(z + r - r \cos \theta)}{h}\right\} \times \ell r d\theta \quad (10)$$

The total interaction energy is the sum of interactions of all small strips of area dA with the flat surface.

$$E_H^{ef} = 2Kh\ell r \exp\left(\frac{-z}{h}\right) \int_0^{\pi/2} \exp\left\{\frac{-r}{h}(1 - \cos \theta)\right\} d\theta \quad (11)$$

Equation 11 is multiplied by a factor of 2 in order to account for the interaction energy from the lower half of the cylinder (i.e. $-\pi/2 \leq \theta \leq 0$).

The hydration energy decreases rapidly with an increase in θ , provided the radius, r , is large compared to the separation distance. Under these circumstances, Verwey and Overbeek (1948) proposed the following approximate expression which has subsequently been used by Sparnaay (1959) and James and Williams (1982).

$$\cos \theta = 1 - \frac{\theta^2}{2} \quad (12)$$

The error caused by the use of this expression in the case of electrostatic interaction between two parallel cylinders was found to be less than 1 percent for $\kappa r \geq 2.5$ (Sparnaay, 1959). The error in

the hydration energy expressions is expected to be even smaller than that because of the short range nature of the hydration force. On substitution:

$$E_H^{ef} = 2Kh\ell r \exp\left(-z/h\right) \int_0^{\pi/2} \exp\left(\frac{-r\theta^2}{2h}\right) d\theta \quad (13)$$

or,

$$E_H^{ef} = 2Kh\ell r \sqrt{\frac{2\pi h}{r}} \exp\left(-z/h\right) \left\{ \Phi\left(\frac{\pi}{2} \sqrt{\frac{r}{h}}\right) - \Phi(0) \right\} \quad (14)$$

where $\Phi(x)$ is the Error Function, $\text{erf}(x)$.

If the radius of the kaolinite edge is taken as 82 nm, and the maximum value of h is around 2 nm for divalent ions as reported in the literature, then the value of $\frac{\pi}{2} \sqrt{r/h}$ is found to be 10.

The function $\Phi\left(\frac{\pi}{2} \sqrt{r/h}\right)$ approaches unity for the values of $\frac{\pi}{2} \sqrt{r/h}$ greater than around 4.

Therefore with an error of less than 0.003%,

$$\Phi\left(\frac{\pi}{2} \sqrt{\frac{r}{h}}\right) - \Phi(0) \approx \frac{1}{2} \quad (15)$$

and Equation 14 simplifies to

$$E_H^{ef} = \sqrt{2}Kh\ell \sqrt{\pi hr} \exp\left(\frac{-z}{h}\right) \quad (16)$$

The interaction in force terms is obtained by differentiating the energy expression with respect to separation distance z resulting in

$$F_H^{ef} = \sqrt{2}K\ell \sqrt{\pi hr} \exp\left(-z/h\right) \quad (17)$$

Edge-Edge Hydration Force

The E-E interaction of kaolinite platelets is represented by the interaction between two parallel cylinders of equal radii. Following Derjaguin's approach, the surfaces of the cylinders are assumed to be divided into 'ribbons' of width $r d\theta$ and length ℓ . If the distance of closest approach between the two parallel cylinders is given by z , then the variable distance Z between the cylinders as a function of angle θ is given by

$$Z = z + 2r(1 - \cos \theta) \quad (18)$$

Combining Equations 5, 8, and 18, and using the procedure described in the previous section, the hydration force between two interacting edges of the kaolinite platelets is obtained as

$$F_H^{ee} = K\ell\sqrt{\pi hr} \exp\left(-\frac{z}{h}\right) \quad (19)$$

Born Repulsion

Face-Face Born Repulsion Force

For $r \gg z$, the Born repulsion in force terms between a sphere and a flat plate can be determined by differentiating Equation 20 with respect to separation distance to give

$$F_B = \frac{Ar\sigma^6}{180z^8} \quad (20)$$

In the case of additive power potential, Derjaguin (1934) expressed the force $F(z)$ between a sphere and a flat plate, which are a distance z apart at their closest approach, in terms of energy per unit surface area between two flat parallel plates $E(z)$ which also are a distance z apart.

$$F(z)_{\text{Sphere-Plate}} = 2\pi r E(z)_{\text{Plate-Plate}} \quad (21)$$

Equation 21 is valid for any type of force law, whether attractive, repulsive or oscillatory, so long as the range of interaction and separation distances are much smaller than the radius of the sphere

(Israelachvili, 1991) or cylinder. Equations 20 and 21 give the Born repulsion energy between two flat plates as

$$E_B^{ff} = \frac{A\sigma^6}{360\pi z^8} \quad (22)$$

The Born repulsive force between two parallel flat plates is then given by

$$F_B^{ff} = \frac{A\sigma^6}{45\pi z^9} \quad (23)$$

Edge-Face Born Repulsion Force

The following expression is obtained for the interactive force between an edge and a face surface using Equation 22 and following the procedure adopted in the previous section.

$$F_B^{ef} = \frac{A\sigma^6 \ell r}{22.5\pi} \sum_{n=0}^N \frac{\Delta\theta}{\{z + r - r \cos(n\Delta\theta)\}^9} \quad (24)$$

Equation 24 is found to be convergent within 5% of the final value for N equal to 550. The Born repulsion force for a E-F association could therefore be evaluated precisely using a simple computer code for larger values of N.

Edge-Edge Born Repulsion Force

The Born repulsive force between two interacting edges of kaolinite platelets is obtained using Equations 8, 18, and 22, which is given by

$$F_B^{ee} = \frac{A\sigma^6 \ell r}{22.5\pi} \sum_{n=0}^N \frac{\Delta\theta}{\{z + 2r - 2r \cos(n\Delta\theta)\}^9} \quad (25)$$

Again, Equation 25 is convergent for large values of N, and the Born repulsion could be estimated conveniently using a simple computer code.

Electrical Double Layer Force

Face-Face Electrical double Layer Force

For two parallel plates with the same potential (i.e. $\psi_1 = \psi_2$) the electrical double layer interaction in force terms is given by Gregory (1975) as

$$F_E^{ff} = 32\epsilon\kappa^2 \left(\frac{kT}{ev}\right)^2 \left\{ \tanh\left(\frac{ev\psi_1}{4kT}\right) \right\}^2 \exp(-\kappa z) \quad (26)$$

Edge-Face Electrical Double Layer Force

Using the principle of LSA and Derjaguin's integration procedure the interactive force between a flat plate and a cylinder of radius r is given by

$$F_E^{ef} = 32\sqrt{2}\epsilon\ell\kappa\sqrt{\pi\kappa r} \left(\frac{kT}{ev}\right)^2 \tanh\left(\frac{ev\psi_1}{4kT}\right) \tanh\left(\frac{ev\psi_2}{4kT}\right) \exp(-\kappa z) \quad (27)$$

Edge-Edge Electrical Double Layer Force

Combining Equations 4, 8, and 18 and using Derjaguin's integration procedure gives the following final expression for the interaction between edges of two kaolinite platelets.

$$F_E^{ee} = 32\epsilon\ell\kappa\sqrt{\pi\kappa r} \left(\frac{kT}{ev}\right)^2 \left[\tanh\left(\frac{ev\psi_2}{4kT}\right) \right]^2 \exp(-\kappa z) \quad (28)$$

van der Waals Forces

Face-Face van der Waals Force

The attractive energy per unit area between two plates of thickness, δ , at a distance, z , from each other is given by Equation 1. Since the thickness of the kaolinite platelets is much

larger than the equilibrium separation distance between them, the last two terms of Equation 1 can be neglected to give

$$E_v^f = -\frac{A}{12 \pi z^2} \quad (29)$$

Equation 29 has been used by Williams and Williams (1982) and Yong et al. (1979) to represent the attractive energy between two flat plates. The force of attraction can be obtained by differentiating Equation 29 with respect to separation distance.

$$F_v^f = -\frac{A}{6 \pi z^3} \quad (30)$$

Edge-Face van der Waals Force

Israelachvili (1991) developed the attractive energy expression for two parallel cylinders of length ℓ and radii r_1 and r_2 , separated by a distance z , at their closest approach as

$$E_v^{ef} = -\frac{A\ell}{12\sqrt{2}z^{3/2}} \left(\frac{r_1 r_2}{r_1 + r_2} \right)^{1/2} \quad (31)$$

The interaction between a cylinder and a flat plate is a special case of the interaction between two parallel cylinders, and it could be obtained in force terms by setting $r_1 \gg r_2$ and equal to r in Equation 31 and differentiating it with respect to separation distance, z .

$$F_v^{ef} = -\frac{A}{8\sqrt{2}} \left(\frac{\ell}{r^2} \right) \left(\frac{r}{z} \right)^{5/2} \quad (32)$$

Edge-Edge van der Waals Force

The following expression is obtained in force terms for E-E interaction by setting $r_1 = r_2 = r$ and differentiating Equation 32.

$$F_v^{ee} = -\frac{A\ell}{16r^2} \left(\frac{r}{z} \right)^{5/2} \quad (33)$$

It is important to note that the expressions for the hydration forces, electrical double layer forces (except F-F interactive force), and Born repulsion are original derivations made in this study, while expressions for van der Waals forces are given by others (Israelachvili, 1991; Sparnaay, 1959). However, the ratios of E-F to E-E interactive forces among all four forces considered in this study remained constant with a multiplying factor of $\sqrt{2}$ for all the expressions developed in this work as well as the ones reported by others on van der Waals forces. This consistency also provides an indirect verification of the expressions derived in this work.

EXPERIMENTAL INVESTIGATION

Materials

A sample of kaolinite clay provided by Dry Branch Kaolin Company, Georgia, was used in this study. A portion of the clay was dispersed in distilled water and the particle size analysis was performed using a Brinkmann particle size analyzer. The results of this analysis displayed the polydisperse nature of the sample with a mean size of 1.64 μm . X-ray diffraction analysis of the sample showed two dominant peaks (3.58 angstroms and 7 angstroms), which characterized the sample as pure kaolinite with a moderate crystallinity (Weaver, 1994). Solid spherical particles made of soda-lime silica glass, supplied by Potters Industries Inc., were used as media grains for particle attachment. More than 90% of the particles were true spheres having a size range of 0.43 mm to 0.6 mm and a nominal size of 0.5 mm. Prior to their use, the glass beads were cleaned of adsorbed materials using a procedure described by Tobiason (1987).

Experimental

Detachment experiments were done in two steps: an attachment step followed by a detachment step. A kaolinite suspension of 33.33 mg/L was prepared and equilibrated with an

electrolyte of desired ionic strength and pH prior to its use in detachment experiments. A glass column of 27 mm diameter was packed with 175 grams of glass beads. Before being packed the glass beads were equilibrated overnight with a solution of same chemical composition as that of the influent kaolinite suspension. The suspension was then filtered through the column for 4 hours for particle attachment onto media grains. During filtration all effluent was collected for later mass measurements. Immediately after the particle attachment was completed the column was backwashed under fluidized conditions with a 20% bed expansion and all backwash water was collected. Mass measurements were carried out for each sample and the percent detachment (as mass) was then determined by mass balances.

RESULTS AND DISCUSSION

Depending upon the chemistry of the suspending medium, kaolinite platelets may flocculate in E-E, E-F, or F-F modes of interaction. The adsorbed organic coatings have also been reported to influence the predominant mode of interaction (Dennett et al., 1996). An E-E flocculation presumably leads to chains and/or sheets of associated platelets, whereas an E-F flocculation produces cardhouse type flocs (Flegmann et al., 1969). The platelets may also associate in F-F fashion to produce card pack aggregates (Rand and Melton, 1977). Therefore, using kaolinite platelets, variations in the interparticle modes of association in response to changes in the chemistry of the suspending medium may determine the nature of the resulting deposits during particle attachment. The detachment of particles deposited in a porous media may be affected by the nature of the deposit undergoing erosion (Mahmood et al., 1995). A knowledge of the dominant modes of interaction of kaolinite platelets as a function of solution pH may therefore be helpful in mechanistic understanding of the phenomenon of detachment.

Theoretical expressions for the F-F, E-F, and E-E modes of association in kaolinite platelets, which were developed in the previous section, have been used to explain the experimental results semi-quantitatively. In theoretical force calculations a value of 2.6×10^{-20} J has been used for the Hamaker constant, whereas Born repulsion is estimated using a collision diameter of 0.5 nm. In quantification of the hydration force a characteristic decay length of 0.9 nm has been used in conjunction with a value of 1.6×10^6 N/m² for the hydration force constant. Figure 3 shows the total interactive force in nanoNewtons between kaolinite platelets held in F-F, E-F, and E-E modes of association as a function of separation distance (nm) at pH 3. Force calculations show that all three modes of interaction have finite depths of primary minima. The depth of the primary minimum is the least for an E-E mode of interaction, whereas a very deep primary minimum is observed in the case of a F-F interaction as depicted by Figures 4 and 5. The depth of the primary minima and therefore the magnitude of the adhesive force follows the sequence $FF > EF > EE$. In a F-F interaction a very deep primary minimum (Figure 5) indicates a very strong association, but a large force barrier that extends to a separation distance of around 35 nm (Figure 3) limits interparticle approach and hence attachment. At this pH a relatively small fraction of the particles colliding in a F-F mode could therefore be expected to surmount this barrier. The E-E mode of interaction in Figure 3 also shows a repulsive force barrier at close approach that extends up to a separation distance of around 15 nm and makes this mode of association less likely too. The E-F orientation shows an attractive force between the two platelets at all separation distances. The E-F attractive force becomes prominent at a considerably large separation distance of greater than 20 nm and then continues to increase monotonically until the equilibrium separation distance (primary force minimum) is reached. A monotonic increase in attractive force can be explained on the basis of electrokinetic properties of the kaolinite platelets. At pH 3, the edges of a platelet are positively charged, whereas the face surface carries a negative

charge. The oppositely charged edge and face surfaces attract each other at large separation distances enabling the particles to come close enough for van der Waals forces to become operative as well. The superposition of long-range electrostatic attractive forces and van der Waals attractive forces gives rise to a much stronger net long-range attraction. Included in the repulsive forces are the hydration force and Born repulsion, which are both short range in nature and decay within distances around 2 to 5 nm from the surface. Force calculations presented in Figure 3 suggest clearly that the most likely mode of association at pH 3 is E-F.

Figure 6 shows total interactive forces between kaolinite platelets at pH 5. At a constant ionic strength of 0.004 M (using NaCl), force calculations for the F-F interaction showed no change with variations in pH, which is consistent with the nature of charge on platelet faces. The origin of charge on platelet faces is because of isomorphous replacement and there is no evidence for a pH dependent charge density at the basal surfaces of kaolinite particles (Rand and Melton, 1977). Under these circumstances, a F-F interaction should be independent of solution pH. A repulsive force barrier in the case of an E-E mode of interaction is still evident from Figure 6 but its height and extent have decreased with an increase in pH. The E-F orientation shows an attractive force at all separation distances suggesting that E-F is also the preferred mode of interaction at pH 5.

At pH 7, which is close to the isoelectric point of the edge surface, both E-F and E-E interactions produce almost identical force curves as shown in Figure 7, although the depth of the primary minimum (and therefore the adhesive force) for an E-F interaction is still larger than that of an E-E interaction. Particle associations in both E-E and E-F modes of interaction are therefore likely to occur at this pH.

At pH values higher than the isoelectric point of an edge surface, the attractive force is due mainly to van der Waals forces since the electrostatic attraction arising due to opposite signs

of charges on platelet faces and edges diminishes. The negatively charged edge and face surfaces give rise to repulsive electrical double layer forces. Total force calculations at pH 9 are presented in Figure 8, where all three modes of interaction display repulsive force barriers and their heights decrease in the order $F-F > E-F > E-E$. The repulsive force barriers present in all three modes of interaction will not only keep platelets from flocculation in any of the F-F, E-F, or E-E modes of interaction but also from attachment to other negatively charged surfaces. This hypothesis was validated experimentally by depositing kaolinite platelets in porous media columns. Solid spherical particles made of soda-lime silica glass were used as media grains in the column experiments. A sample of experimental results on particle attachment at pH 4.02 and 8.05 is shown in Figure 9, where C and C_o represent effluent and influent suspension turbidities. The normalized filter effluent turbidity (C/C_o) at pH 8.05 was found to be greater than 0.8 as compared to a value of less than 0.1 at pH 4.02, which demonstrates highly dispersive characteristics of the kaolinite platelets at pH 8.05. Also, in rheological studies of aqueous clay suspensions Rand and Melton (1977) found kaolinite platelets to be very dispersed at pH above around 8. The experimental observations made in this study as well as those reported in the literature (Rand and Melton, 1977) are consistent with the extended DLVO theory presented in this paper.

In a particular chemical environment, the predominance of one mode of association does not constitute a complete absence of the other modes of association. For instance, under dilute acidic conditions the predominant mode of interaction is E-F, however platelets approaching in E-E and F-F orientations may also cause flocculation if the driving force is sufficiently large to surmount the force barrier. Though small, the occurrence of relatively less likely modes of association at a particular pH cannot be ignored. F-F associations are expected to be independent of solution pH since the negative charge on the basal planes of the kaolinite platelets originates due to isomorphous substitutions. The extent of F-F associations may therefore be the same at all

pH values under constant ionic strength conditions. The edge charge on the other hand originates as a result of broken bonds at the edges and it is a function of pH. Therefore, the extent of E-F and E-E associations should essentially be dependent on pH. At low values of pH the E-F interactions are highly favorable and a high filtration efficiency is achieved (see Figure 9 for pH 4.02). The relative abundance of F-F interactions may be small at low values of pH because the total number of E-F associations is very large. As the pH is increased the edge charge becomes less positive up to the isoelectric point of the edge surface and then increasingly more negative while the face charge stays the same. This affects both E-F and E-E interactions while keeping the colloidal forces unaltered for the F-F associations. At high values of pH the total number of interparticle associations is significantly low. It may therefore be expected that the relative abundance of the F-F associations increases gradually as the pH is increased.

It is important to note that the quantification, and therefore comparison, of net adhesive forces among the three modes of interaction was made possible by inclusion of short range effects into the DLVO theory. The extended DLVO theory presented in this publication predicts finite depths of primary minima, as shown in Figures 4 and 5, in contrast to unrealistic infinitely deep primary minima obtained by others (James and Williams, 1982; Kuo and Matijevic, 1978) considering DLVO interaction energies alone.

In one set of experiments, the ionic strength of the suspended particles was kept constant at 0.004 M using sodium chloride while the suspension pH was varied from 3 to 8 during particle attachment. The attached particles were detached using a backwash water of constant chemical composition. The ionic strength of the backwash water was kept constant at 0.0006 M (using NaCl) while the pH was fixed at 7.2 in each experiment. During particle detachment the filter media was fluidized with a bed expansion of 20%. The results of detachment experiments are shown in Figure 10, where the percent detachment (as mass) has been plotted as a function of

attachment pH. The release of kaolinite platelets was found to be dependent on pH of the influent suspension and a maximum in percent mass detachment was observed at a pH value around 5. A similar trend of kaolinite erosion from a bed simulating a stream was observed in a subsequent study using a tilting flume under uniform flow conditions (Ravisangar, 1996). The observed behavior of kaolinite detachment can be explained using the theoretical micromechanics model developed in this study. The heteropolar kaolinite platelets may associate in different geometric modes depending upon pH of the interacting medium. The most likely association at pH 3 is E-F, where a positively charged edge is attracted electrostatically by a negatively charged basal face. The electrostatic attraction in conjunction with van der Waals forces creates relatively stronger and longer range attraction between an edge and a face of two interacting platelets and causes them to attach. It is worthwhile to emphasize that when the two surfaces are oppositely charged the electrical forces become attractive, and instead of countering the van der Waals forces (as they do in the case of similarly charged surfaces), they reinforce them instead giving rise to a long-range, strong net attraction.

As the pH is raised above 3, the edge charge becomes less positive, mitigating the attractive electrostatic contribution to the total E-F attractive force. Adhesive forces holding the clay platelets in an E-F mode of interaction therefore become weaker, which makes particle release to occur more easily and causes percent detachment to increase as observed in Figure 10. Also, a rise in pH causes the interparticle mode of interaction to change from E-F to E-E. An E-F association is inherently stronger than an E-E association, which is evident from the expressions developed for the hydration forces, electrical double layer forces, Born repulsion, and van der Waals forces. Total force calculations show that the depth of the primary minimum for an E-E orientation is 31 nN as compared to a depth of 44 nN in the case of an E-F association at pH 5. The greater depth of primary minimum for an E-F interaction than that of an E-E association

suggests that the particles which attach in an E-E orientation could be detached more easily as compared to those attached in an E-F mode. Also, the force calculations show that as the pH is increased from 3, the fraction of attached particles held in an E-E mode of association increases. This gradual increase in contribution of the weak E-E associations contributes further to the increase in percent detachment up to pH around 5.

At higher values of pH (above 7) kaolinite particles are very stable and only a small fraction can attach. The relative contribution of F-F associations to the total interparticle associations may be expected to increase as the pH is raised. The predominance of F-F structures at higher pH values has been suggested also in the literature. Based on the dense and compact nature of settled kaolinite deposits in conjunction with their low water content, Dennett (1995) suggested that the associations at high pH ($> \text{pH } 7$) are predominantly F-F. F-F associations are very strong and give rise to card pack structures. Particles held in this mode of association will resist the eroding forces much more than those held by other modes of association. The observed decrease in percent mass detachment at high pH values may therefore be attributed to the increased fraction of F-F associations. The F-F associations give rise to dense, tightly packed flake-like structures (Rand and Melton, 1977; van Olphen, 1977), whereas E-E and E-F interactions result in voluminous, three dimensional, cardhouse-like structures of high void ratio (van Olphen, 1977). It is hypothesized that the dense, flake-like structures attached to a surface will protrude less into the fluid boundary layer as compared to voluminous, cardhouse like structures. Under conditions of constant fluid shear stress, the compact F-F structures may experience relatively smaller hydrodynamic forces than those experienced by the cardhouse like voluminous structures and hence will detach less.

Limitations of space has necessitated a focus on theoretical developments in this paper. Additional experimental validation of the approach is given in Mahmood (1996) and will be presented in a future publication.

CONCLUSIONS

It is realistic and reasonable to analyze interactions between kaolinite particles considering their actual platelet-like shape instead of making use of oversimplifying assumptions of particle sphericity. The microscopic force model developed on the basis of hexagonal platelet like shape of kaolinite particles was found to be consistent with experimental observations on attachment and detachment of kaolinite particles.

The microscopic force analysis showed that the total interactive force between the two interacting particles varies drastically with their geometric shape. Under constant chemical conditions the three geometric modes of interaction (E-E, E-F, and F-F) of the kaolinite platelets showed significantly different total force curves and the magnitude of the adhesive force was found to vary with the type of interparticle mode of association. The depth of the primary minima and therefore the magnitude of the adhesive force followed the sequence $F-F > E-F > E-E$. The expressions developed for the E-F mode of interaction for hydration forces, Born repulsion, electrical double layer forces, and van der Waals forces showed stronger interactive forces than those between the E-E mode of association by a factor of $\sqrt{2}$.

The release of kaolinite platelets under constant chemical conditions during particle detachment was found to be dependent on the pH of the suspension used during particle attachment. Kaolinite platelets showed a maximum in the percent detachment at an attachment pH around 5. The variations in the interparticle adhesive forces, both within a specific mode of

interaction and due to changes in the predominant modes of interaction with pH were found to explain the maximum percent detachment observed experimentally at a pH value around 5.

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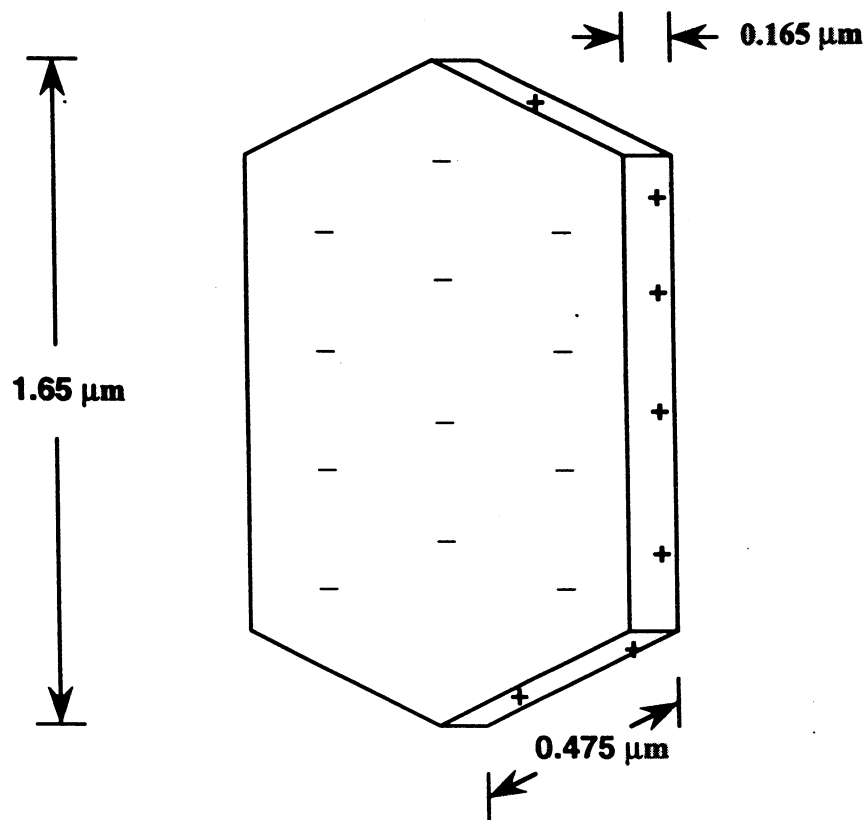


Figure 1. A representative kaolinite platelet.

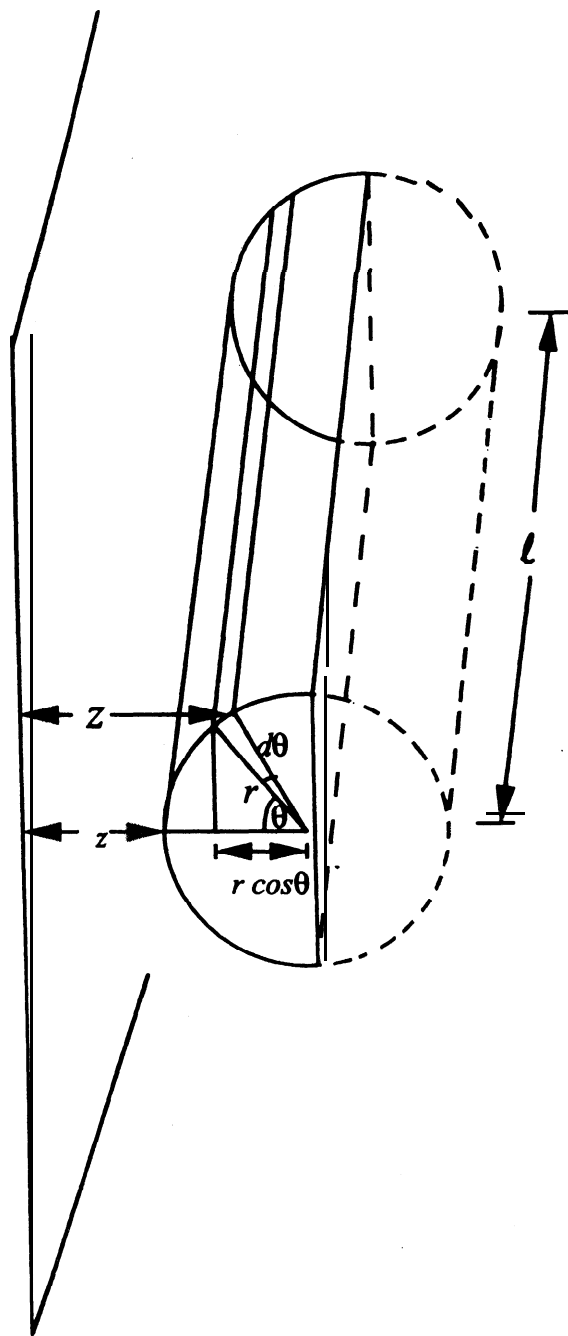


Figure 2. Geometry of a flat plate-cylinder interaction.

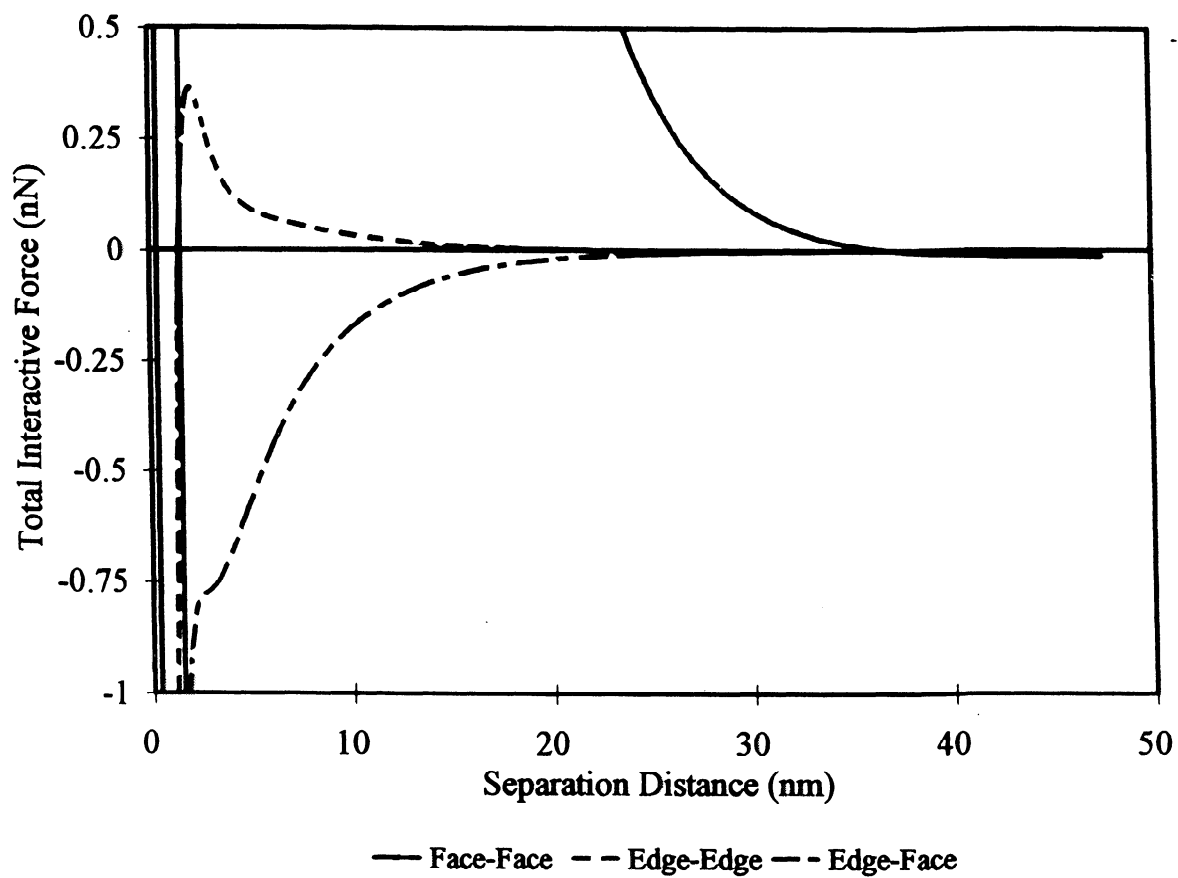


Figure 3. Total interactive force between kaolinite platelets at pH 3.

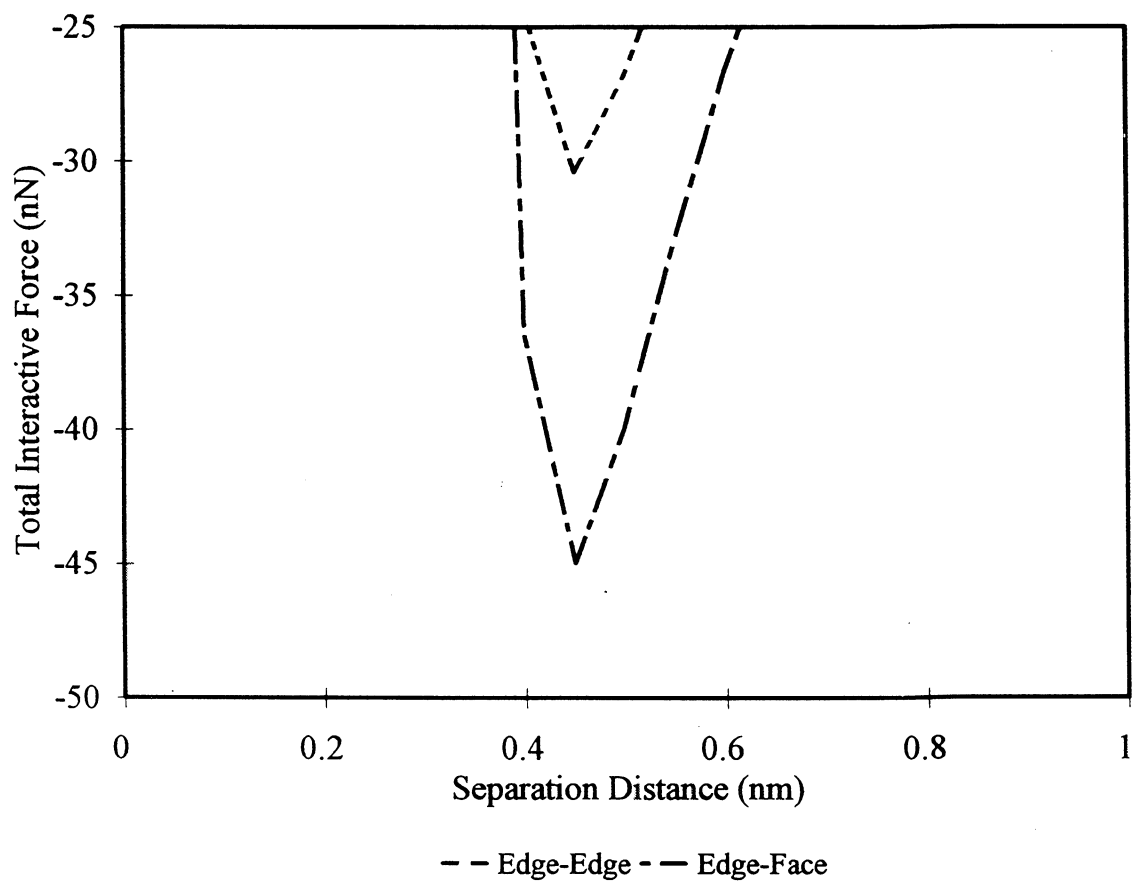


Figure 4. Adhesive forces for E-F and E-E modes of interaction at pH 3.

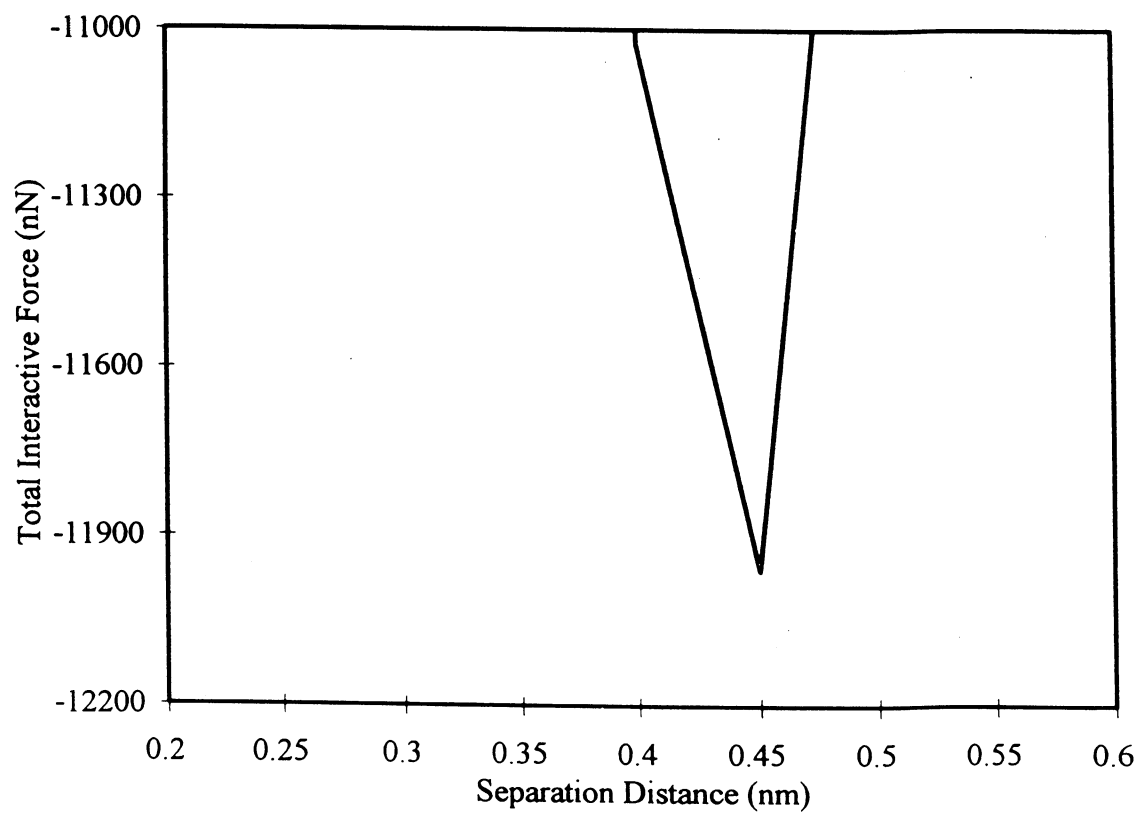


Figure 5. Adhesive force for a F-F association at pH 3.

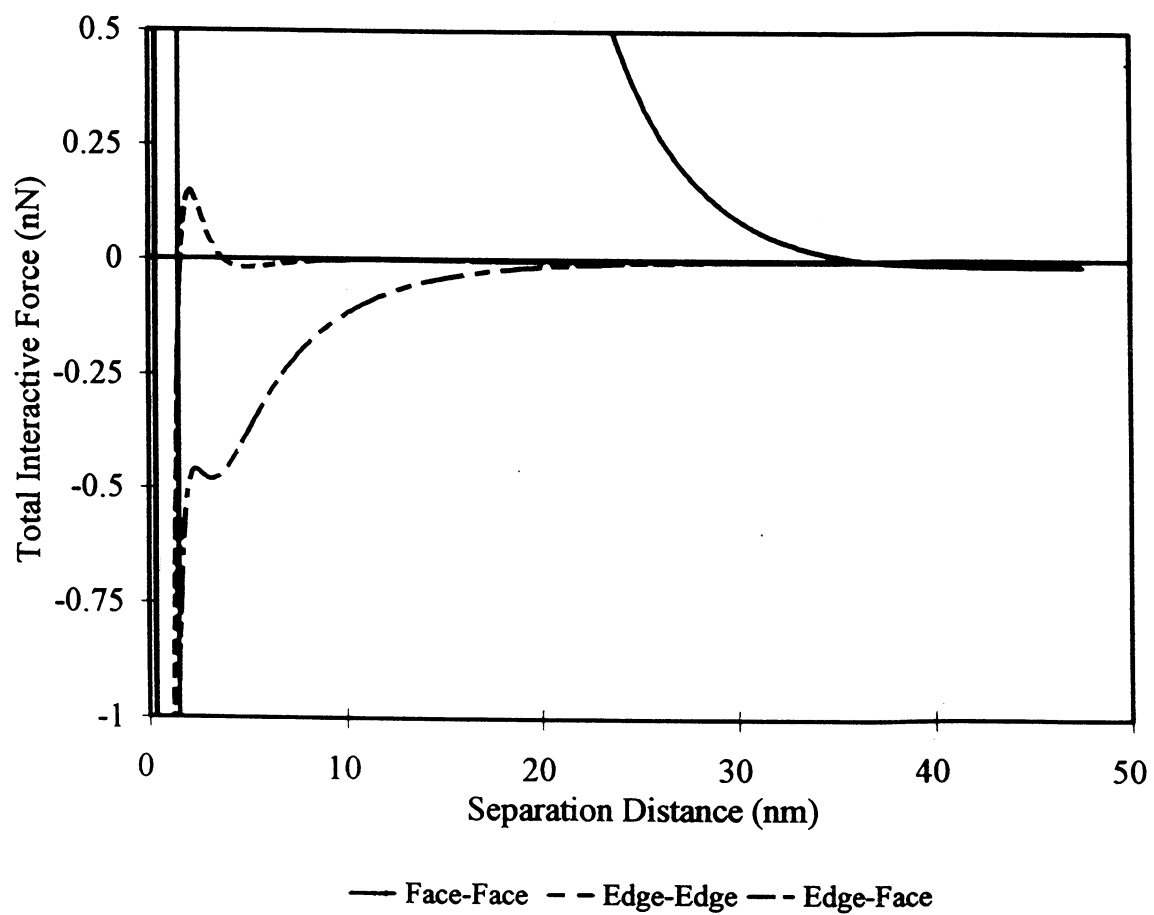


Figure 6. Total interactive force between kaolinite platelets at pH 5.

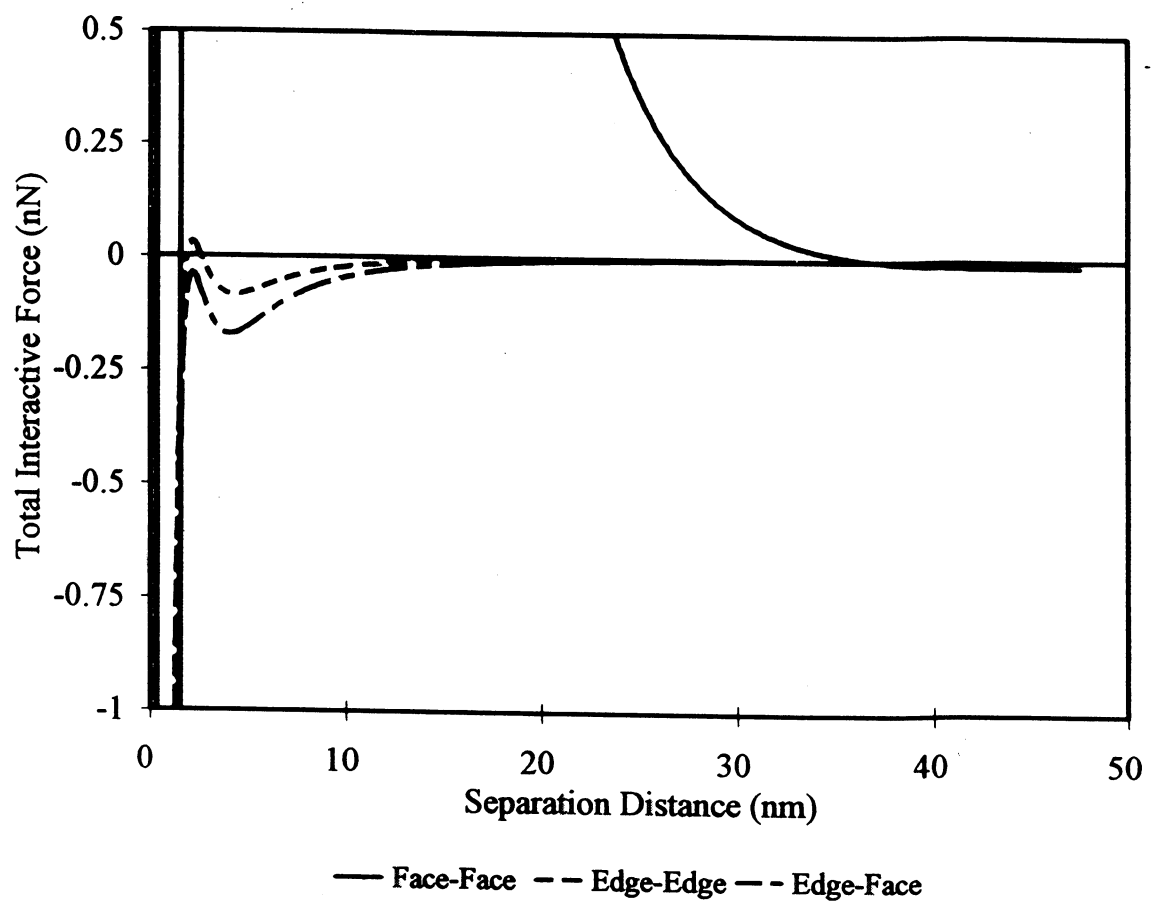


Figure 7. Total interactive force between kaolinite platelets at pH 7.

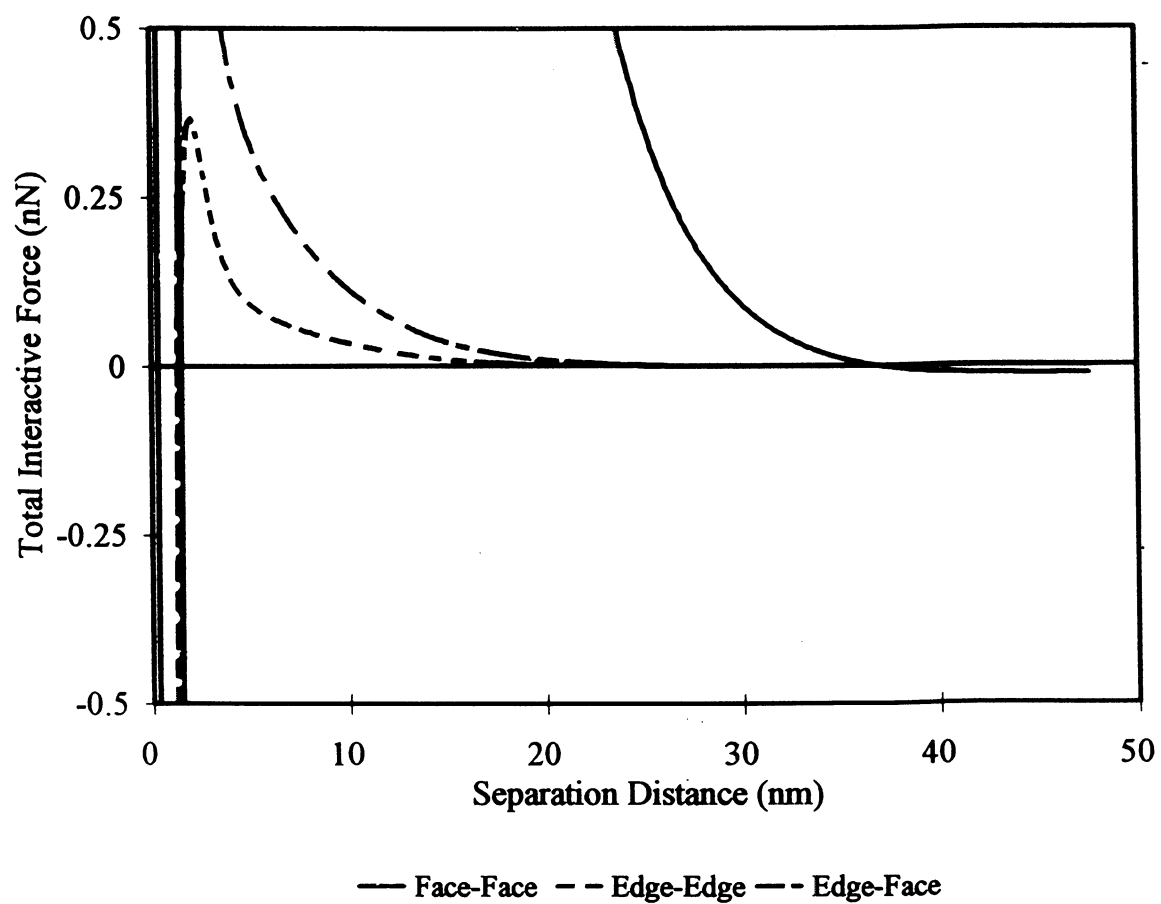


Figure 8. Total interactive force between kaolinite platelets at pH 9.

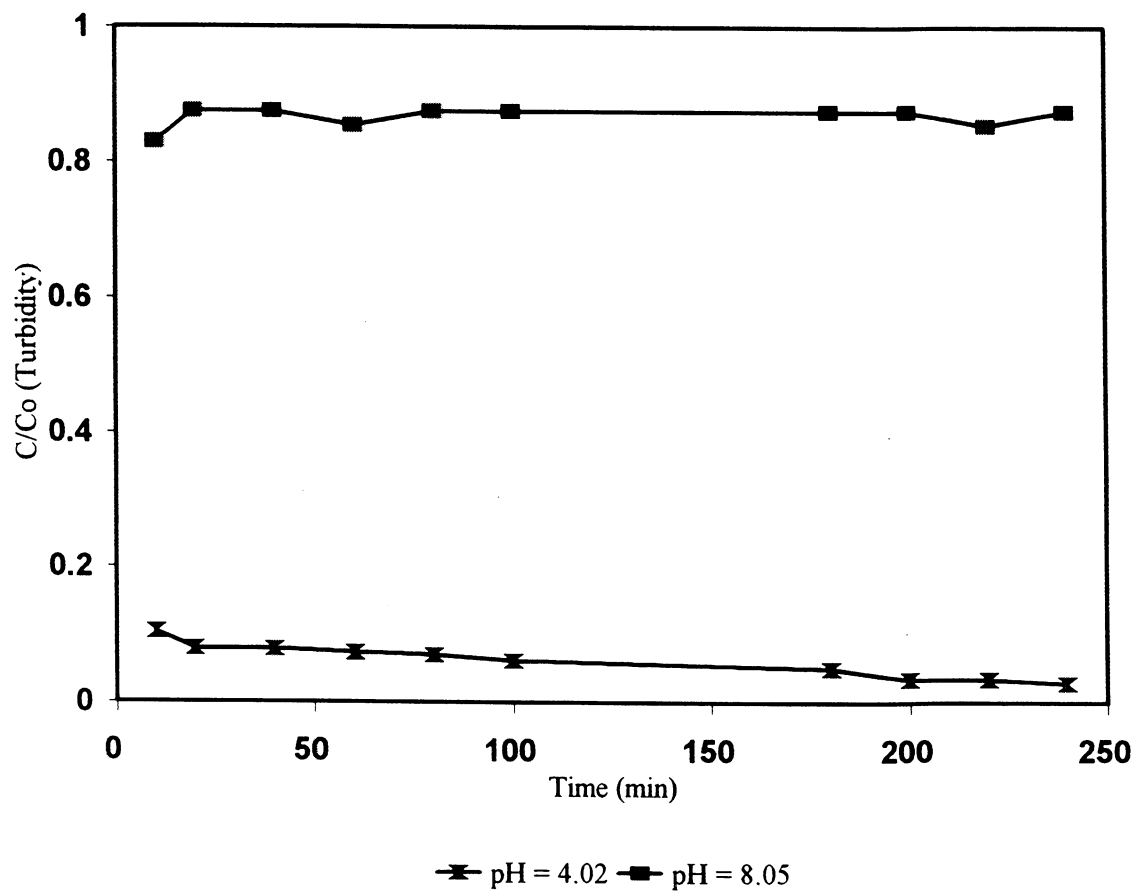


Figure 9. Filtration of kaolinite at constant ionic strength.

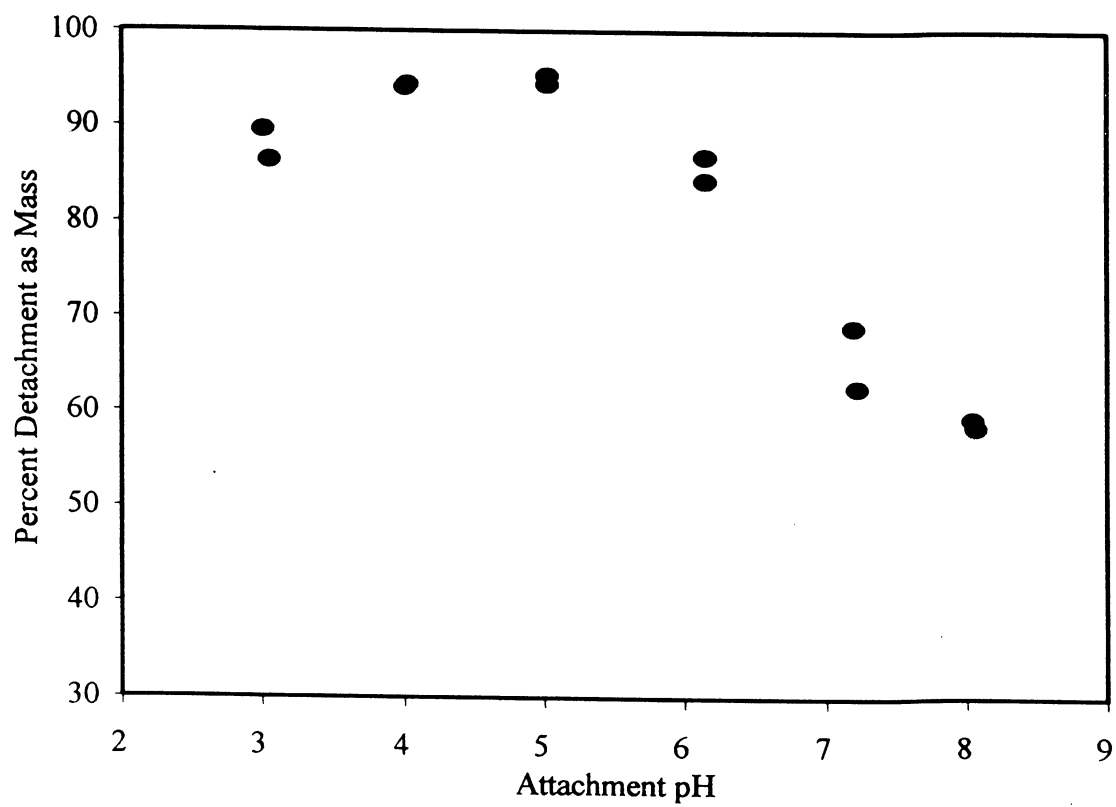


Figure 10. Effect of attachment pH on detachment of kaolinite platelets.

